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NO_x Storage and High Temperature Soot Oxidation on Pt–Sr/ZrO_2 Catalyst

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Abstract NO_x storage–release and soot oxidation have been studied using strontium promoted zirconia with different surface areas. It was found that the amount of the adsorbed NO_x increases with the increase of the support surface and Sr concentration up to 20 wt% Sr. Introduction of platinum has no effect on the amount of NO_x stored, but improve soot oxidation due to recycling of NO to NO_2. A combination of oxidation catalyst with NO_x storage materials enables to lower the temperature of 20% soot conversion up to 100 °C in comparison with un-catalyzed soot oxidation.

Keywords Soot oxidation · Diesel particulate filter · NO_x storage/release · Zirconia · Strontium

1 Introduction

The emissions of nitrogen oxides (NO_x) and particulate matter (soot), produced by diesel-powered vehicles, represent a major environmental and health issue in highly populated areas. In Euro 5 and 6 emission standards for cars and light trucks, which are implemented in 2009 and 2014, respectively, level of soot in exhaust should be decreased almost five times in comparison with Euro 4 regulations (http://www.dieselnet.com/standards/eu/).

Soot can be removed by placing a filter in the exhaust line. The particular matter collected in the filter has to be periodically or continuously removed to avoid clogging, which is normally achieved by soot combustion. Without the catalyst and using oxygen as the oxidant the solid carbon (soot) that forms the particular matter can only be burnt at temperatures above 600 °C [1, 2]. However, supplying heat costs fuel and uncontrolled soot combustion can lead to high temperature gradients and, therefore, can damage the filter. Alternatively catalytic soot combustion can be applied. The largest challenge arising here is, however, the solid–solid contact between catalyst and soot since in realistic conditions this interaction between catalyst and soot is very limited and, therefore, catalyst efficiency is low [1, 3].

It is possible to bypass the problem of the poor contact if the role of the catalyst is only to provide active gaseous species during regeneration conditions (rich period) and restore them back during normal lean driving period. There are two principle active gaseous species that can be used to combust the collected soot. Oxygen is the most obvious, since it is present in large quantities (5–10%) in diesel exhaust. Oxygen storage/release materials such as CeO_2 [4], rare-earth modified CeO_2 [5], perovskites [6], and spinel type oxides [7] can provide active oxygen which can initiate soot combustion at temperatures around 450 °C which is significantly lower than that in the case of an un-catalyzed soot oxidation [4].

Contrariwise, nitrogen dioxide (NO_2) is known to be a more powerful oxidant than oxygen: it can convert soot to CO and CO_2 at temperatures as low as 275–300 °C [8, 9]. A possible strategy is to use a combination of an oxidation catalyst and a NO_x storage material which will store the NO_x at temperatures of diesel engine operation, i.e., below 300 °C, as nitrates and release it during the phase of high temperature regeneration [10]. In this case an oxidation catalyst will oxidize NO into NO_2 and, subsequently, the NO_2 will convert soot into CO and CO_2 and back to NO which can participate in the next soot oxidation event.

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Since NO conversion to NO_2 is thermodynamically unfavorable at temperatures above 400 °C, it has to be recycled to NO_2 with a very high efficiency; platinum is, therefore, most commonly added as an oxidation catalyst [9, 11, 12].

Traditionally, Ba and K are the most reported NO_x storage systems, since they were also applied in the gasoline three-way systems [11–14]. CeO_2, ZrO_2, and La_2O_3 were also reported to store certain amounts of NO_x, which can be used for the soot oxidation [15–17]. Recently, NO_x assisted soot oxidation has been reported for a series of alkali-earth oxides supported on Al_2O_3, where Sr and Ca-based systems have shown the highest efficiency [18].

In this work we have studied the NO_x storage–release and soot oxidation on strontium promoted zirconium oxide with different surface areas. Platinum was further introduced to enhance oxidative function of the catalysts.

2 Experimental

2.1 Materials

ZrO_2 (provided by Alfa Aesar, a Johnson Matthey Company, 99% purity) with two different surface areas of 51 and 90 m^2/g was used as support material. Supported catalysts containing 2.5–20 wt% $Sr(NO_3)_2$ (provided by Riedel-de Haën, 99% purity) were prepared by incipient wetness impregnation of a sieved fraction (0.065–0.35 mm) of the support with an aqueous solution of strontium nitrate. Prior to impregnation, the supports were dried in an oven at 200 °C for 5 h. Impregnated supports were dried at room temperature for 12 h and heated in air up to 120 °C with a heating rate of 5 °C per minute and kept at 120 °C for 2 h.

A total of 1 wt% Pt was introduced by incipient wetness impregnation using $Pt(NH_3)_4Cl_2{\cdot}H_2O$ (provided by Alfa Aesar, a Johnson Matthey Company, 56.4% purity) salt as precursor. Synthetic Printex-U soot from Degussa S.A. was used as a model soot whose characteristics are reported elsewhere [19].

2.2 NO_x Storage–Release Cycles and NO_x Storage Capacity

For the storage–release of NO_x FTIR Thermo Nicolet Nexus spectrometer using Spectratech diffuse reflectance accessory equipped with a high temperature cell was used. OMNIC software was used to collect and process the spectra. Pfeiffer ThermoStar Mass spectrometer was coupled to the FTIR unit. In the standard experiment approximately 50 mg of sample was placed into the high-temperature ceramic cell. Further temperature was increased from 200 to 600 °C with a 100 °C steps in a flow of 20% O_2 in He (30 mL/min). With the increase of the temperature, bulk nitrate decomposes with the release of NO_x from the sample. The MS signal of evolving NO is used to calibrate MS signal, since the exact amount of nitrates in the starting sample is known.

The sample obtained after the previous calcination step was treated at 200 °C with a flow of 800 ppm of NO + 20% O_2 in He (30 mL/min) and NO is adsorbed on the catalyst with the formation of nitrates and nitrites. At the same time FTIR spectra were collected every 2–5 min until no changes were observed in the spectra. Afterwards the flow of NO was switched off and the temperature was increased from 200 °C until 600 °C with 100 °C step in 20% O_2 in He mixture (30 mL/min). The decomposition of the nitrates was monitored by MS. The amount of the released NO_x can be used to estimate the share of the storage component involved into the NO_x storage using following formula:

$$\text{Storage capacity}\ (\%) = \frac{\text{Amount of desorbed NO}_x\ (\text{mmol/g}_{\text{cat}})}{2\ \times\ \text{amount of storage cation}\ (\text{mmol/g}_{\text{cat}})}$$

2.3 Soot Oxidation

Soot oxidation is studied by temperature programmed reaction method. Soot is mixed with catalyst and silicium carbide as dilutant in proportion of 1:20:120 with a spatula in order to obtain a loose contact mode. A total of 200 mg of sample is packed between two quartz wool plugs in a tubular quartz reactor (5 mm internal diameter). Reactor is heated from 40 to 900 °C with a heating rate of 5 °C/min in a flow of 20% O_2 in He (50 mL/min). Reaction products are analyzed by Balzer mass spectrometer. Soot conversion at each temperature and selectivity of soot oxidation to CO_2 can be quantified using the areas under CO- and CO_2-signals and assuming complete soot combustion at 900 °C:

$$\text{Conversion}\ (\%) = \frac{S_{CO}(T) + S_{CO_2}(T)}{S_{CO}^{tot} + S_{CO_2}^{tot}} \times 100$$

where $S_{CO}(T)$ and $S_{CO2}(T)$ represent areas under the CO and CO_2 curves at selected temperature T and S_{CO}^{tot} and$S_{CO_2}^{tot}$ represent areas under the CO and CO_2 curves at 900 °C

$$\text{Selectivity}\ (\%) = \frac{S_{CO_2}^{tot}}{S_{CO_2}^{tot} + S_{CO}^{tot}} \times 100$$

3 Results and Discussion

3.1 NO_x Storage–Release

During the storage stage NO is adsorbed by the alkaline earth oxides from the mixture of 800 ppm of NO + 20%

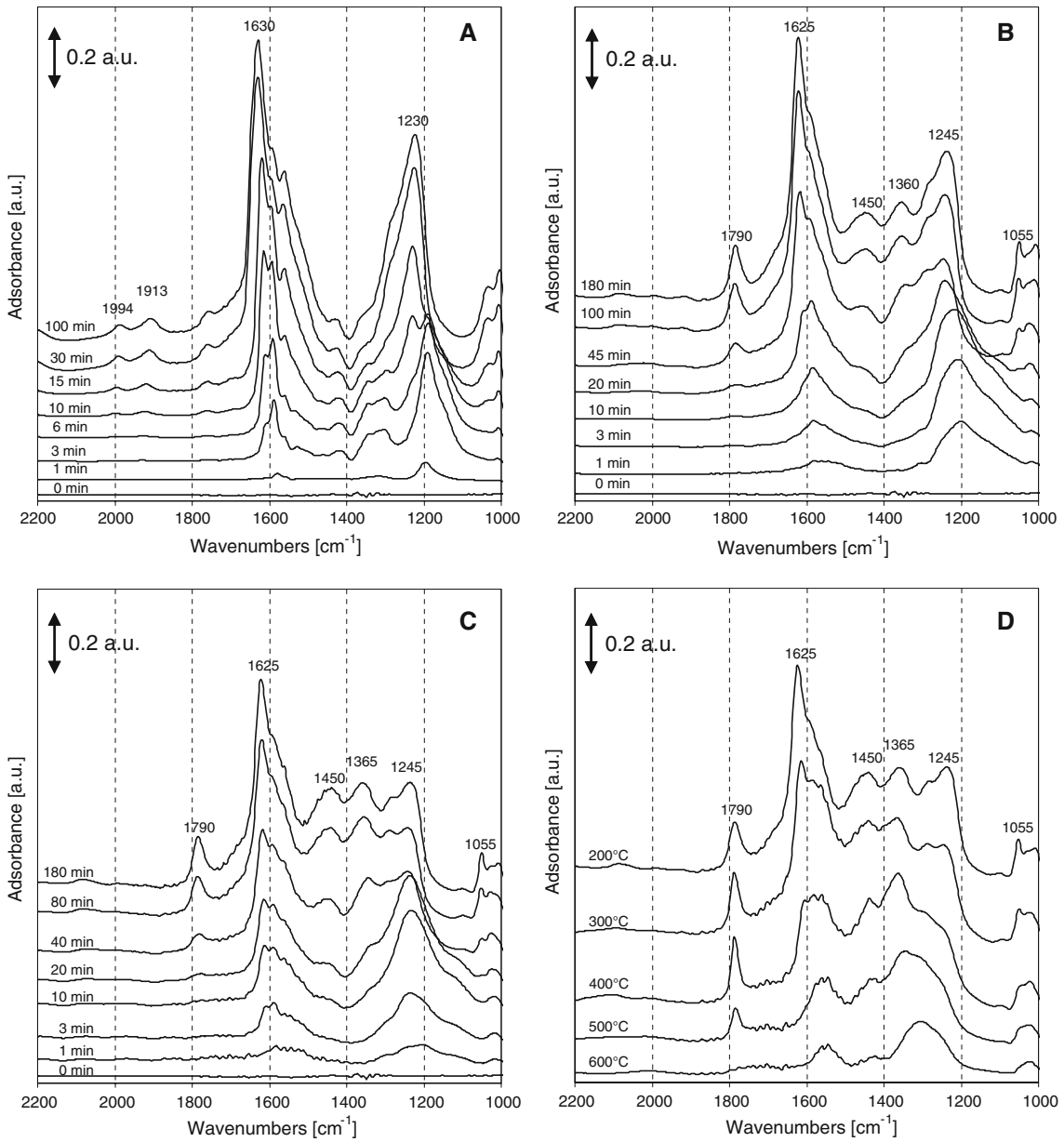

Fig. 1 FT-IR spectra upon adsorption of 800 ppm NO in 20% O_2 in He mixture on ZrO_2 (**a**), 20%$Sr(NO_3)_2/ZrO_2$ (**b**), and 1%Pt–20%$Sr(NO_3)_2/ZrO_2$ (**c**) at 200 °C after calcination at 600 °C and desorption spectra for 1%Pt–20%$Sr(NO_3)_2/ZrO_2$ sample (**d**)

O_2 in He at 200 °C, while the FTIR spectra are recorded. The evolution of the spectra with the increase of the adsorption time for pure ZrO_2 and two supported samples (Sr/ZrO_2 and Pt–Sr/ZrO_2 obtained after decomposition of corresponding precursors in air at 600 °C) are shown on Fig. 1a–c. The desorption spectra for Pt–Sr/ZrO_2 sample after saturation with NO_x is shown on Fig. 1d.

It is possible to observe that already after few minutes bands, characteristic to nitrite species appear in the region 1000–1800 cm^{-1} [20, 21]. Further these bands progress and at higher exposure times new adsorption bands grow at expenses of nitrite bands, which can be assigned to nitrates in a monodentate, chelating, and bridging configurations until saturation is reached. Noteworthy, according to the FTIR results most of the NO_x is adsorbed within the first 20–30 min. For pure ZrO_2 pronounced bands at 1630, 1230, and 1010 cm^{-1} can be observed. These bands and a minor band at around 1300 cm^{-1} can be associated with the formation of bidentate nitrites and nitrates (chelating or bridging configurations) [17, 20]. For Sr containing sample (Fig. 1b) additional bands at 1450, 1360 and 1055 cm^{-1} appear which can be assigned to the ionic nitrates. Weak band at 1790 cm^{-1} can be assigned to the formation of nitrosyl M–ON^- or M–NO^- species and can be correlated

Table 1 NO_x desorption characteristics and storage capacities of different samples determined using FTIR–MS results

Sample	Surface area (m^2/g)	NO_x desorbed (μmol/g)	Storage capacity (%)
ZrO_2	51	6	–
ZrO_2	90	32	–
20%$Sr(NO_3)_2/ZrO_2$	51	169	17.9
20%$Sr(NO_3)_2/ZrO_2$	90	319	33.8
1%Pt–20%$Sr(NO_3)_2/ZrO_2$	51	168	17.9
1%Pt–20%$Sr(NO_3)_2/ZrO_2$	90	297	31.4

to the presence of Sr on the surface, since the intensity of this band increases with increasing of the Sr concentration (spectra for samples with different Sr concentrations are not shown here for the sake of brevity). With addition of platinum (Fig. 1c) the intensities of the bands at 1450 and 1360 cm^{-1} become somewhat higher indicating the enhancement of the formation of ionic nitrate species.

The decomposition and desorption of stored nitrates can be also observed in FTIR spectra (Fig. 1d). With the increase of the temperature above 300 °C the intensity of the bands decreases significantly and at 600 °C most of the bands disappears, indicating almost complete decomposition of stored nitrates. However, some minor bands characteristic for bidentate or ionic nitrate species remain even at 600 °C. The results of NO_x storage–release for different systems are summarized in Table 1. Noteworthy, the amount of desorbed NO_x and storage capacity increase significantly with increasing surface area of the support. This can be related with a better distribution of Sr and its higher availability for the NO_x storage on the support with higher surface area and, therefore, storage capacity increases. Addition of Pt has no effect on the amount of stored NO_x and according to FTIR data only promotes the formation of ionic nitrate species on the expense of bridged and bidentate nitrates. One might find such a result as rather unexpected, since, for example, in the works of Nova [22] significant positive effect of Pt on the NO_x storage capacity in Ba/Al_2O_3 system was reported. This contradiction can, however, be explained by the difference in the storage conditions. In the works of Nova NO_x storage was performed at 350 °C, where thermodynamic equilibrium between NO and NO_2 is strongly shifted towards the formation of nitrous monoxide. Therefore, the addition of Pt is essential for converting of NO to NO_2 and formation of nitrates. At the temperature used in this study (200 °C) NO_2 is still present in significant amounts in the equilibrium with NO. Therefore, Pt is not that essential for the formation of nitrates. It should also be pointed out that in the works of Nova et al. [22] the adsorption experiments were performed with the mixture of NO in He with no or very small amounts of oxygen (NO/O_2 ratio of 1:4), while in our case experiments are conducted with a large excess of oxygen, which also favors the formation of NO_2.

3.2 Soot Oxidation

With the increase of the temperature the nitrates start to decompose with the release of nitrogen dioxide that reacts with the soot forming CO, CO_2 and back to nitrogen monoxide. The results of the soot oxidation for different catalysts are summarized in Table 2, where temperature of 20% soot conversion as well as amount of soot converted up to 500 °C are given to provide the comparison between different systems. Selectivities of soot conversion to CO_2 are also shown. For the un-catalyzed soot oxidation (no stored nitrates present in the system) the temperature of 20% soot conversion is quite high, around 580 °C. After the introduction of even small amounts of stored nitrates into the system the temperature of the soot oxidation decreases quite significantly (~33 °C for sample containing 2.5% $Sr(NO_3)_2$). With further increase of the concentration of nitrates the temperature decreases even further and for the most active sample 20%$Sr(NO_3)_2/ZrO_2$ it is 508 °C, which is 72 °C lower than that for the un-catalyzed reaction. The amount of soot converted before 500 °C also increases gradually with the increase in the Sr concentration and reach 16.7% for catalyst with 20%$Sr(NO_3)_2$ versus 6.5% for pure ZrO_2.

Platinum alone also does not improve the soot oxidation (Table 2, sample $1\%Pt/ZrO_2$) and only increases the selectivity of the soot conversion to CO_2 by oxidizing the formed CO. However, a significant improvement in terms of catalytic activity as well as selectivity was observed when Pt was added to the storage component. Combination

Table 2 Performance of the catalysts in soot oxidation

Catalyst	$T_{20\%}$ (°C)	$Conv_{500\ °C}$ (%)	S_{CO_2} (%)
ZrO_2	576	6.5	84
$1\%Pt/ZrO_2$	570	6.7	91
2.5%$Sr(NO_3)_2/ZrO_2$	547	9.2	91
5%$Sr(NO_3)_2/ZrO_2$	538	11.2	85
20%$Sr(NO_3)_2/ZrO_2$	508	16.7	79
1%Pt–20%$Sr(NO_3)_2/ZrO_2$	475	32.0	93

Reaction conditions: temperature from room temperature to 900 °C, heating rate of 5 °C/min in a flow of 20% O_2 in He (50 mL/min). Soot:catalyst:SiC ratio of 1:20:120, loose contact

of both storage component and Pt lower the temperature of soot oxidation ~100 °C and the amount of soot removed before 500 °C increases from 6.5 to 32%.

4 Conclusion

It was shown that Sr supported on ZrO_2 can be used as a NO_x storage–release material which can be applied for the diesel soot removal. High surface area of the support is necessary to ensure high NO_x storage efficiency. The addition of platinum has no effect on the amount of NO_x stored, but it is crucial for the recycling of NO to NO_2 and in combination with NO_x storage component significantly increases the efficiency of overall soot oxidation.

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